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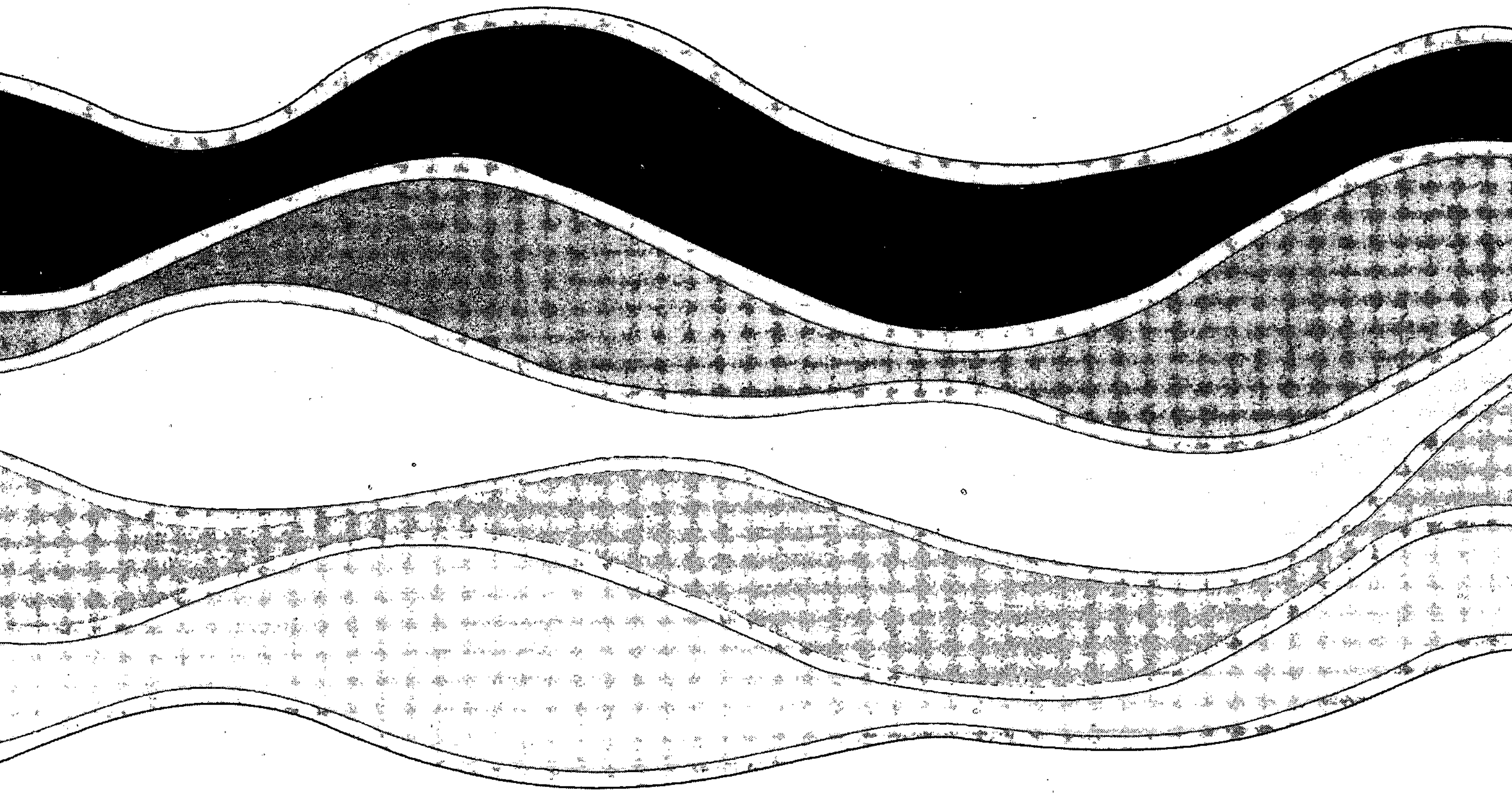

PREPARATION OF A REFERENCE MATERIAL FOR ORGANIC CONTAMINANTS IN PRECIPITATION BY LARGE-SAMPLE EXTRACTION

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NWRI Contribution No. 93-73

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MANAGEMENT PERSPECTIVE

This report describes a method for collection of large volumes of precipitation and a procedure for their processing by large-sample extraction in order prepare a "realistic" reference material for use as a QA/QC material by analytical laboratories producing data for environmental monitoring, regulatory and research purposes.

Precipitation samples have been used in development of the technique. This matrix has been shown to be a significant transport mechanism in long-range deposition of organic contaminants to water systems. The reported technique could readily be applied to most other aqueous matrices of environmental concern (eg. Hudson Bay, Northern Rivers, Niagara River, Hamilton Harbour, Great Lakes, etc.).

SOMMAIRE À L'INTENTION DE LA DIRECTION

Ce rapport décrit une méthode pour prélever l'eau des précipitations en grand volume ainsi qu'une marche à suivre pour le traitement par extraction de gros échantillons afin de préparer du matériel de référence «réaliste» qui doit servir à l'AQ/CQ dans les laboratoires où sont faites des analyses dans le cadre de la surveillance du milieu, de la réglementation et de la recherche.

Des échantillons d'eau de précipitations ont servi à la mise au point de la technique. On a montré que cette matrice est une vecteur important de transport à distance de contaminants organiques qui se déposent dans des réseaux hydrographiques. La technique dont il est fait état est directement applicable à la plupart des autres matrices aqueuses d'intérêt environnemental (p. ex., baie d'Hudson, rivières boréales, rivière Niagara, port d'Hamilton, Grands Lacs, etc.).

ABSTRACT

The determination of ambient levels of hydrophobic organic contaminants in aqueous matrices suffers from the lack of a standard reference material (SRM), prepared from "real" environmental matrices, for use as a QA/QC material by environmental analytical laboratories responsible for providing data for monitoring, surveillance, and regulatory activities. Such reference materials cannot be prepared in an aqueous matrix by virtue of the properties of the analytes. This report describes a technique for preparation of a reference material in the "next best" matrix, an organic solvent. This is the matrix in which such analytical determinations are ultimately made.

The technique serves as an example of how the Goulden Large-Sample Extraction (GLSE) process may be used to prepare reference materials of most environmental aqueous matrices. It allows processing of a 1000 L sample within a period of fifteen working hours, producing twenty litres of extract material. This amount of extract is sufficient to provide one hundred 200 mL subsamples for use as a reference material for a particular program.

RÉSUMÉ

Il est difficile de déterminer la concentration naturelle de contaminants organiques hydrophobes dans des matrices aqueuses du fait qu'il n'existe pas de substance de référence normalisée qui soit préparée à partir de matrices «réelles» qui provienne du milieu, et qui puisse être utilisée pour l'AQ/CQ par les laboratoires d'analyse environnementale qui doivent produire les données aux fins du contrôle, de la surveillance et de la réglementation. Ces substances de référence ne peuvent pas être préparées à partir d'une matrice aqueuse à cause des propriétés des mélanges à analyser. Ce rapport fait état d'une technique de préparation d'une substance de référence dans la «meilleure matrice de remplacement», soit un solvant organique. Il s'agit de la matrice dans laquelle ces analyses sont faites en fin de compte.

La technique illustre de quelle façon le procédé Goulden d'extraction de gros échantillons peut servir à la préparation de substances de référence à partir de la plupart des matrices aqueuses de l'environnement. Elle permet le traitement d'un échantillon de 1000 L en 15 heures de travail et produit 20 litres de substances extraites. On peut préparer 100 sous-échantillons de 200 mL de substances de référence en vue de l'application d'un programme précis.

CONTENTS

1. INTRODUCTION : RATIONALE FOR THE EXPERIMENT

1.1 The Need for an RM for the Determination of Organic Contaminants in Water

The availability of reference materials (RMs), certified reference materials (CRMs) and standard reference materials (SRMs) is of great importance for laboratories conducting analyses of environmental materials as they provide a means of internal and external QA/QC necessary to lend credence to analytical data. This is of extreme importance in expensive, large-scale programs involving many laboratories which may or may not be using similar analytical protocols (eg. international programs such as the Canada/United States Air Quality Agreement (1)). Of equal importance is the "preservation" of data in a form that is referenced or normalized to an agreed upon standard so that comparisons between contemporary and future data are not, as has frequently occurred in the past, artifactual reflections of improved analytical methodology and analytical knowledge.

The environmental analytical industry has expanded greatly during the last two decades due to the problem of environmental pollution by xenobiotic organic chemicals resulting from, primarily, activities of petrochemical, agrochemical and pulp and paper industries (2).

Despite expansion in this area of analytical methodology and instrumentation, a corresponding increase in useful QA/QC procedures for the determination of organic contaminants in water has not been forthcoming. This is largely a result of the properties of the analytes concerned. The majority of "target" organic contaminants listed in various "Priority Substance" lists (3,4,5) are hydrophobic organochlorine compounds. The hydrophobic properties of these compounds precludes their use in preparation of an aqueous phase RM as they tend to adsorb to the surface of container materials. Many may undergo hydrolytic, oxidative or auto-decomposition reactions on storage in aqueous matrices (6). As these contaminants generally require some degree of preconcentration for their determination at ultratrace levels, a further practical restraint in providing an aqueous phase RM is the immense volume of water requiring storage and distribution.

1.2 Current QA/QC Approaches to the Determination of Organics in Water

This problem is currently being addressed by the use of "surrogate standards" (an internal standard technique) or by the "spiking" technique (generalized standard addition technique, (7)). In examining environmental aqueous matrices, a major drawback to the standard addition technique is the "aging" or equilibration of the analyte with matrix components. This process cannot be done effectively with aqueous samples as the equilibration necessarily allows other processes to affect analyte concentrations in the sample [1.1].

No studies of ambient organic contaminant levels in water have had available a reference material for inter- and intra-laboratory QA/QC purposes. Data produced and used for distribution and trend studies in these exercises may be questionable. This may be especially so in studies which have used "spiked" solvent (eg. "pure" water or solvent) solutions as a QA/QC material. Such approaches serve in testing instrument/operator performance but do not reflect the effect of sample matrix on analytical cleanup, fractionation and detection procedures. General requirements of reference materials are described elsewhere (8).

1.3 An Alternate Approach to RM Preparation for Determination of Organics in Water

An alternative approach to providing such a reference material is to prepare solvent extract of a matrix of interest. The contaminants of interest are ultimately determined in a solvent extract to satisfy general requirements for gas chromatographic (GC) and high performance liquid chromatographic (HPLC) separations. The stability of most hydrophobic contaminants in an organic solvent (usually dichloromethane (DCM)) or other low molecular weight hydrocarbons or aromatics) is generally accepted as being greater than that in an aqueous matrix. Extracts, containing analytes and interferences particular to the matrix, would be representative of the particular aqueous matrix concerned and would provide a more realistic test of laboratory analytical capabilities. The volume of reference material requiring storage would be substantially reduced. The solvent, DCM, used in large-sample extraction is appropriate in this application as it can easily be "solvent exchanged" with other less volatile solvents commonly used in GC and HPLC work.

The extract obtained from a particular matrix would contain "target" compounds at ambient levels. Through interlaboratory comparisons, "real" detectability in laboratory performance could be assessed and ambient concentrations assigned on a statistical basis.

This report describes the development of a "very large-sample extraction" (VLSE) technique (9) for preparation of a large quantity of extract from a precipitation matrix. This matrix was chosen due to its relatively non-complex chemical nature, the existence of various studies of contaminant levels in the matrix (10,11,12), and its importance in international environmental issues concerned with the deposition of airborne toxic chemicals (13,14).

The approach taken in this study centers on modifying the Goulden Large-Sample Extraction (GLSE) technique (6,15,16) for the production of large volumes of extract from very large (1000 L) samples of rainwater. Normally, the objective in large-sample extraction (LSE) is the reverse, the production of an analytically acceptable minimum quantity of solvent extract of a large aqueous sample.

2. EXPERIMENTAL

2.1 Sample Collection

The general philosophy observed in this study was that the results need not be strictly quantitative. The intent was to collect a large quantity of extract representative of the matrix within a reasonable time period. As a reference material for "target" contaminants, the main consideration would be to quantitate what was present in the extract or added to it. The material would also be useful for identification of unknown contaminants. For this reason, and to preserve the "virgin" nature of the extracts, surrogate standards were not added to the extraction process to monitor extraction efficiency (15-19) except for a single "sacrificed" portion of the sample.

Rainwater samples were collected on two occasions; during the Fall of 1990 and the Summer of 1991. The sampling was intentionally conducted during weather patterns dominated by air movements originating from the south (Gulf of Mexico) and passing through the heavily industrialized area of the US northeastern states (eg. the Ohio Valley) before reaching the Niagara Peninsula. The collection site was located in Grimsby, Ontario. The site closely borders a major highway and a railway line. Polynuclear aromatic hydrocarbons (PAHs) from rubber "dust" and diesel fumes were thus expected to be a major contribution to contaminants in the samples collected. The site also lies downwind from the Hamilton industrial complex. Rainfall during the two precipitation events was collected from the roof of a glass greenhouse into a series arrangement of five stainless steel barrels (200 L @) through a custom-made sampling arrangement which allowed sequential filling of the barrels **(Fig.1)** (20). This arrangement allowed a comparison to be made between contaminant levels in initial rainfall and those of the later stage of the event. Approximately 1000 L of rainfall were collected per event. Rainfall from the first event (November, 1990) was collected without cleaning of the roof surface as this would provide a "worst-case scenario". The second sampling (August, 1991) was conducted after high pressure water "jet" cleaning and rinsing of the roof surface the day before the predicted event **(Fig.2)**. Detergent washing of the surface was not used as surfactant residue would be readily extracted (21).

The rainfall sample from the first collection was immediately transported to CCIW and processed without clarification. The second collection was immediately transported to CCIW, clarified by high-speed continuous-flow centrifugation and processed by solvent extraction.

2.2 Preparatory Aspects

2.2.1 Collection Barrel Cleaning

"Clean" 200 L stainless steel barrels were rinsed with ~4 L of "organics-free" water (Millipore MQ2 water purification system with activated carbon "organics polishing" cartridge), followed by two rinses with ultrapure methanol (≈ 500 mL each rinse) for removal of polar organic compounds and water, and finally with ≈ 500 mL of DCM to remove less polar, hydrophobic organic compounds. The solvent rinses were pumped out of the containers into waste containers. For the second collection, the barrels were rinsed with pressurized tap water (sprayed into the inverted containers).

2.2.2 Sample Clarification

The sample from the November 1990 collection was clarified by an on-line filtration technique (22) using precleaned (solvent rinsed, dried at 110 °C) "organic binder-free" glass fibre filters (Nucleopore, 142 mm OD, 0.7 / pore diameter, P/N 211825). The contents of each barrel were sampled from the top ≈ 20 cm of the liquid level by frequent adjustment of the sampling probe (**Fig.3**). Experience with this sample showed that cleaning of the roof surface was desirable and that clarification of the sample by in-line filtration was not a feasible process. Therefore, high-speed continuous-flow centrifugation (17) was used to clarify the sample from the second collection.

2.2.3 Sample Degassing

Both samples contained high concentrations of dissolved gases (air). The problem this poses in continuous-flow solvent extraction has been recognized (6,15,16). For samples received below room temperature, degassing was accomplished by on-line sample preheating (15,16). In the first collection, the more difficult of the two in this respect, the situation was improved by adjusting the degree of mixing and recovering solvent carryover from the separator trap (**Fig.3**). Aspirator vacuum degassing, sonication (using the GLSE accessory tube (16)), and overnight venting of the sample were tested.

2.2.4 QC Samples

Prior to the first collection, a series of solvent samples were prepared to monitor tainting of the extracts by contamination from various aspects of the processing technique. These samples are described in **Table I.**

2.3 Sample Processing

Samples were processed by a modified large-sample continuous-flow solvent extraction technique incorporating the Goulden Large-Sample Extractor (GLSE) (15,16). The following description refers to the development of the VLSE (very large sample extraction) technique; the finalized procedure is described in the **Appendix.**

Extraction effluent was treated off-line using prototype solvent recovery equipment to reduce the content of dissolved DCM in the extraction effluent before discharge to waste.

In this VLSE technique, an "oversized" amount of solvent was used to increase recovery of less hydrophobic contaminants (log Kp < 3) and to provide the desired amount of extract. This augmentation was done on-line in order to expose all solvent to the matrix and to minimize the degassing problem. A diagram of the processing arrangement is shown in **Fig.3.** Extract was collected through a sintered glass filter funnel (Buchner-type, Ace Glass Inc., P/N 7184- 10) supporting a precleaned (methanol and DCM rinsed) glass fibre filter (Whatman, type GF/F, 4.7 cm) with mild suction (≈ 5" Hg water aspiration) **Fig.4,** directly into 4 L amber glass reagent bottles (fitted with Teflon-lined caps) previously used to contain only the original high purity solvents. The funnel/bottle seal was made by wrapping the funnel joint with teflon tape and clamping the funnel in place.

2.3.1 Optimization of Extraction Conditions

The samples were processed at various flow and agitation rates to determine optimum processing conditions. Otherwise, the general considerations of the "standard"

GLSE technique were followed (16). Sampling rate, initial DCM "charge", and stirring rate were varied during work with the first sample to optimize conditions for expedient sample processing of the second sample.

During the later stage of processing the first 1000 L sample, a 50 L aliquot was "sacrificed" to allow estimation of the extraction efficiency using the optimized processing conditions. This was accomplished using on-line addition of the "Niagara River Protocol" surrogate standards (6,15-19).

All DCM used in this study was of the same Lot Number (# AT 519, Burdick and Jackson, P/N 300-04, "High Purity" grade) and was tested by GC/AED analysis before use for its suitability in large-sample extraction (16).

2.3.2 Compositing and Storage of Extracts

The volume of extract to be collected from the entire 1000 L sample was 20 L. Four L of extract were collected from each barrel (200 L) of sample. The five extracts from each sample collection were composited in a 20 L Pyrex carboy with a withdrawal tap (Corning, 5 gal, "Pyrex", P/N 1230) and mixed by overhead stirring (Caframo, model RZR50 stirrer) with a stainless steel paddle (Cole-Parmer, 4-bladed, Stn Stl, 40 mm OD, P/N L-04370-13; shaft, Cole-Parmer, Stn Stl, 10 cm OD, 500 mm L, P/N L-04370-02) for 1 h. The mixture was then redistributed to the five 4 L containers and stored, layered with ≈1 cm of water to reduce evaporation of solvent, at ≈ 5 °C.

2.4 Analysis of Extracts

For the purpose of the following discussion, a **preconcentration factor [1]** is defined as:

volume of sample (L) / volume of solvent extract from preconcentration (L),

a **concentration factor [2]** is defined as:

volume of solvent extract / volume of concentrate* used from preconcentration (L) for analysis (L),

and an **overall concentration factor** [3] is defined as:

volume of sample (L) / volume of concentrate used for analysis (L). [3]= [1] x [2]

All extract samples submitted for analysis had been processed for a nominal preconcentration factor of 50. Overall concentration factors were dependent on subsequent analytical processing. A limited suite of "target" compound analyses were done on the two extracts. Reports of wet precipitation analyses using preconcentration by solvent extraction (12) suggest than an average over-all concentration factor used for determination of target contaminants is 10,000. For ultratrace analytical requirements, an overall concentration factor of 50,000 - 200,000 is used (6,9).

Chlorobenzenes (CBs) were determined on 2000-fold overall concentrates of "blanks" (**Table I**) and samples of the first rainwater collection extract using an analytical protocol for "design" values.

"Blanks" and aliquots of the first rainwater extracts were also analysed ("broad spectrum", semi-quantitative and qualitative: overall concentration factor of 50,000) to provide an overview of the number of ECD-sensitive compounds and PAHs present in the extracts. Aliquots of the first rainwater extract were analysed to quantitate the "Niagara River Protocol" (18,19) suite of organic contaminants (overall concentration factor of 5,000).

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* the term "concentrate" (noun) refers to the material (1-2 mL) resulting from concentration of the extract to low volume by evaporation of solvent and is the solution from which GC samples are taken for analysis.

Aliquots of the second rainfall sample extracts were analysed to determine organochlorine pesticides and industrial materials (OCs) and polychlorinated biphenyls (PCBs). Using this protocol, an overall concentration factor of 10,000 was provided. Extract aliquots from initial and final collection for this rainfall event were analyzed to compare contaminant levels.

A 50 L sample of the first rainfall collection, "sacrificed" for an estimation of extraction efficiency and the MQ2 "blank" were analysed using the "Niagara River Protocol" ultratrace technique (20,21). An overall concentration factor of 30,000 was used in this analysis.

3. RESULTS AND DISCUSSION

The optimized processing technique is described in the **Appendix** along with a summary of operating conditions (**Table A-I**).

3.1 Sample Processing

3.1.1 Sample Clarification

High-speed centrifugation (17) was seen to be the most useful sample clarification technique in comparison with high sample throughput (1 L/min) in-line filtration. With the latter technique, even with a relatively coarse filter, frequent replacement of filter media was necessary due to clogging. This requirement is not attractive for unattended operation of the extract collection process. Centrifugation is only ≈ 85 % effective in removing particles >.45 / in diameter (17). Remaining particulate (POC), colloidal and dissolved (DOM) organic matter not removed in the clarification process do not cause a physical problem in processing samples but can affect recoveries. It can be as, or more, efficacious than the solvent in "sorbing" trace organic contaminants (23-26). Clarification of the first sample by in-line filtration showed that the amount of dry precipitation flushed from the collection surface into the sample was significant enough to interfere physically in processing by causing occasional sample pump seizure

Fine particulate matter passing through the filter and sample pump gradually accumulated in the extractor body, coating the scrubber column (16).

The centrifuged sample from the second collection event was much less problematic. A combination of high-speed centrifugation and filtration, using a larger diameter in-line filter (eg. standard 293 mm OD) and prefilter would likely minimize this problem. The filter could be changed at the same time as an extract was being collected (≈ once per hr) or a sample barrel was being changed (≈ once per 4 hr).

3.1.2 Degassing of Samples

Overnight venting of the samples in the collection barrels was seen to be the most effective means of degassing sample. Degassing by water aspirator vacuum (≈ 30" Hg) tended to implode the container lids and was abandoned as an alternative. Controlled degassing for a few hours with a lower vacuum (eg. 5" Hg) might eliminate this problem if conducted previous to overnight degassing at ambient pressure and might reduce the "layering" effect of dissolved gas observed with simple overnight venting.

On-line sonication using the GLSE accessory tube (16) was ineffective in degassing sample. On-line preheating of sample to 22°C improved sample degassing. This tactic is not recommended beyond this temperature (16).

The "oversize" initial DCM "charge", maintained by on-line solvent compensation (6,15), reduced the problem of dissolved air in the sample. The combination of overnight venting, oversized solvent addition and sample preheating allowed facile operation of the extraction process at the maximum sample-input rate of 1000 mL/min.

3.2 Analytical Results

The data provided in this report are semi-quantitative and qualitative and intended only as preliminary documentation of chemical parameters of the extract material. For this reason, ambient concentrations have not been reported since the "raw" data was sufficient for this purpose.

3.2.1 QC Blanks

CBs were not detected in the QC samples using the "design value" protocol. This was not unexpected as this protocol focusses on the determination of much higher contaminant levels.

The QC "blank" samples **(Table I)** analyzed with a 50,000 fold overall concentration factor showed response in the OC/PCB and PAH analytical schemas **(Tables II,IV, Figures 5, 6)**. These samples contained low-level amounts of a number of "target" compounds as well as many unidentified compounds. The results are somewhat surprising considering the rigorous cleaning procedures used in preparation of the processing equipment, the "virgin" nature of the processing equipment used and the logic of the experimental design **(Table I)**. As the determinations of target compounds were semi-quantitative only, and GC/MSD confirmations of identity were not performed, many of the identifications made may be, in fact, mis-identifications considering the complexity of the chromatograms **(Figures 5,6)**. The contamination by OCs/PCBs appears relatively constant throughout the QC blank series and appears to involve the same compounds (chlorobenzenes and six of a suite of 23 OCs (20)). The contamination is not attributable to the solvent used as a 5.5-fold (≈ 1650 mL / 300 mL) increase in solvent blank II over solvent blank I was not observed. Similarly, a summation effect of contamination from the major possible sources was not seen for the identified compounds in the MQ2 blank. This should contain contaminants from all the sources tested **(Table I)** in addition to ambient contamination of the MQ2 water itself. The inferences drawn from the analysis are that the extract container may be the major contamination source (unlikely, considering the cleaning procedure used and the volatility of the analytes) or that the samples were contaminated, in subsequent analytical processing, by target compounds used in calibration and by QC surrogate standards used in monitoring the efficiency of analytical steps (18). A similar contamination effect was not observed for OCs/PCBs in ultratrace analysis of a second process-MQ2 blank (**Table V**). In this sample, possible contamination by CBs is evident. These low levels (sub ng/L) of target compounds may represent a consistent contamination encountered in this type of analysis. This contamination of procedural blanks by target and other compounds is not critical in comparison with results obtained for the precipitation samples. This is best visualized in **Figures 5, 6** and **Tables II,III,IV** and V and perhaps demonstrates well the care which must be exercised in sampling and analysis for ultratrace determinations. The results of procedural blank analyses have been provided here for the purpose of documentation.These results indicate that a preconcentration of 50 has been used to advantage in this experiment as the procedural blank does not contribute significantly to the sample results.

3.2.2 **Extraction Efficiency**

Surrogate standard recoveries obtained using a "sacrificed" portion of the first rainfall collection (**Table VI**) were typical for this type of analysis (6,15,27, 28). The low recovery of 1,3,5-tribromobenzene reflects losses of the more volatile compounds in the extraction process (related probably to the degassing problem [2.2.3]) but is primarily attributable to volatility loss in subsequent analytical processing. The excellent recovery of δ-BHC (semivolatile) shows the extraction process to be effective even under the "severe" conditions used here for a high processing rate.

3.2.3 **Rainwater Samples**

The "broad-spectrum" qualitative GC/ECD analysis showed a multitude of ECD-sensitive (presumably chlorinated) components of the rainwater matrix, especially in the "B" fractions of the OC/PCB analytical protocol (18) (**Figure 5, a-d**). A similar increased complexity is seen in the TICs (total ion chromatograms, PAH determinations) (**Figure 6**).

The majority of contaminants determined in the rainwater samples (ng/L levels) were PAHs and phthalates, a neutral herbicide (metolachlor), endrin, a-BHC and g-BHC.

Sub-ng/L levels of other OCs/PCBs were determined. These may not be attributable to the rainwater but rather to a consistent low-level contamination of the entire sampling / analytical process (**Tables III, IV, V, VI**).

The duplicate samples of composited extract from the first rainfall collection (5,000-fold overall concentration) showed the presence of PAHs only (**Table VIII**). This is not surprising as the overall concentration factor was low and this collection (wet and dry deposition) is likely to have contained elevated amounts of these compounds **[2.1]**. The results suggest that the compositing process is effective within error limits typical of this type of analysis (27,28).

3.2.4 Contaminant Levels in Initial Rainfall

A current speculation regarding results of atmospheric deposition studies is that the initial fraction of rainfall may act as a "scavenger" of particulate and "dissolved" material in the air below the cloud system, and that rainfall later in the event, the air below the system having been "cleansed", may better represent long-range transport of contaminants. Extract aliquots representing initial and later rainfall collected during first rainfall event did show positive responses for some OCs and PCB congeners. These results are given in **Table VII**; chromatograms are shown in **Figure 8.** The results suggest, considering numbers of detected peaks and levels of quantitated compounds, that there may be a "scavenging" effect in the rainfall collected, with higher contaminant levels in initial rainfall than that collected later. The large volume (200 L) of the sample containers may have allowed dilution of the initial sample in the first collection barrel so that a more definite difference was not seen. The use of smaller containers (eg. 20 L) for collection of initial rainfall might allow investigation of the "scavenging" effect.

3.2.5 General

Analyses performed with lower overall concentration factors (2,000-5,000) provided limited information. Methods using low preconcentration factors are more appropriate for the analysis of highly contaminated waters. The data from this work illustrate the advantage of large preconcentration factors in studying ambient and incipient contamination and its impact on aquatic ecosystem health. The complexity of the chromatograms shown for the rainwater samples illustrates the need for a reassessment of the rationale for focussing entirely on target compounds; the majority of compounds detected in environmental samples by GC separation and conventional detection are unidentified due to a lack of analytical methodology (29).

The samples have been stored as described **[2.3.2]**. The storage of hydrophobic organic compounds in an organic solvent, rather than in water, may be advantageous in that certain depletion mechanisms would be minimized **[1.1]**.

CONCLUSIONS

The technique provides a rapid and facile means of generating a large quantity of extract suitable for use as a reference material in programs assessing the extent of contamination of environmental freshwaters and marine waters by xenobiotic organic chemicals. 1000 L of aqueous sample can be processed in two working days to provide 20 L of extract sufficient for distribution of one hundred 200 mL samples of reference material for use in a particular monitoring program. The solvent (DCM) may be easily solvent exchanged with the less volatile solvents used in GC and HPLC work. The technique can readily be applied on-site.

The process has the potential to be automated. This aspect is currently being studied by the Physical Sciences Department of Mohawk College, (Hamilton, Ontario).

An advantage of this technique over other QA/QC tactics is that the extract may be produced in quantity sufficient for interlaboratory QA/QC purposes while retaining the characteristics (GC-, HPLC-chromatographable components) of the matrix.

The results of analyses conducted suggest that the extraction efficiency of the process, using the "severe" conditions desirable for the objective of this study, were typical for GLSE preconcentration (6,15-19,27,28) and that the compositing technique was adequate. The data also show that large-sample extraction (LSE) can be used to advantage in this application as analytes and coextractables can be preconcentrated well above process contamination levels. The technique provides a basis for application to other aqueous matrices.

This work demonstrates the advantage of large-sample preconcentration in providing ultratrace capability for assessment of the extent of contamination in aqueous matrices. Analyses conducted with low overall concentration factors failed to detect most target contaminants. Target analyses provide only a minuscule glimpse of the extent of contamination by a myriad of organic contaminants in water systems (29). Environmental protection requires a much expanded view, in terms of new analytical methodology providing ultratrace capability in determination of a much more comprehensive suite of organic contaminants than is currently provided commercially.

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APPENDIX: A Technique for Processing Large Samples of Water by Solvent Extraction for the Production of an Extract Reference Material.

Pre-Extraction Considerations

Unless the sample is relatively free of particulate material it should be clarified by high-speed centrifugation [3.1.1]. If the sample has been taken from well-aerated waters it should be degassed by overnight venting or low vacuum water aspiration [3.1.2]. The sample may be further clarified, if necessary, by in-line filtration during the extraction process [3.1.1]. Equipment set-up is shown in **Fig.1**. Details regarding electromechanical equipment, etc. are described elsewhere (16). A summary of operating conditions is given in **Table A-I.**

Summary of the Extraction Procedure

The general aim of the procedure is to provide a 50-fold preconcentration of hydrophobic contaminants in the rainwater matrix from 1000 L of the aqueous matrix to 20 L of DCM extract. This is accomplished by treating the overall process as a series of 50 L (aqueous) / 1 L (DCM) extractions. This serves two purposes. First, the oversized initial DCM "charge" (1 L) improves the recovery of less hydrophobic contaminants (log $K_p < 3$) by providing a high solvent-to-water ratio (SWR) in the GLSE mixing chamber (6,9,16). Secondly, this technique exposes all DCM used in preparation of the reference material to the aqueous matrix and assists in processing aerated samples.

After the initial DCM charge has been added, the sample is pumped into the extractor avoiding uptake of sediment from the bottom of the sample container, and the mixer and solvent compensation pumps are turned on. The heater (degasser) is used if the sample is significantly below 20°C. Mixing characteristics are observed closely and compensation made in sample input rate and agitation rate to achieve or, at least approximate, "ideal" extraction operating conditions (16). Sample is then processed until ≈ 50 L have been extracted, the extract is collected and the process repeated until the entire sample has been processed.

The sample pump should be adjusted to deliver ≈ 1000 mL/min and the solvent compensation pump adjusted accordingly (16). Timing of the process allows estimation of the time required to process 50 L of sample before collection of an extract aliquot and restarting of the process.

Extraction Procedure

- The GLSE and associated equipment are set up as shown in **Fig.3** and **Table A-I.**
- All stopcocks are closed. The filter vent is left open until it has been purged of air by the sample.
- A 1 L aliquot of dichloromethane (DCM) is added to the extractor through the "scrubber column" using a wide- bore glass funnel. The DCM level in the mixing chamber is marked.
- Sample is pumped into the extractor (the in-line filter vent is closed when the filter is purged of air) and as water enters the extractor, timing of the processing is started (with a calibrated sample pump, this provides an estimate of the time required to process 50 L of sample). The stirrer and solvent compensation pump are started (and the sample pre-heater, if required to assist in degassing).
- Stirring of the sample/DCM mixture is adjusted to confine the emulsion to the mixing chamber of the extractor. (Note, this process requires some patience as the mixture does not respond immediately to changes in stirring speed).
- During processing of the first 50 L of sample, the extraction should be checked periodically (15-20 min) to ensure that compensatory solvent is being replaced at the necessary rate (solvent level marking, above) and that phase-mixing is appropriate.
- After ≈ 50 min processing time, the process is stopped (all electrical components turned off) and the phases allowed to "clear".
- A low aspirator vacuum (5-10 mm Hg) is applied to the collection bottle via the filter funnel (with prefilter in place) vacuum port and the extractor drain, with delivery tube attached, is opened and flow is adjusted to balance the filtration speed.

- After collection of extract from the extract drain (and separator trap, if necessary), the filter funnel is removed from vacuum (by disconnection from port), the extract filter is replaced, and the sample in-line filter is replaced. The sample probe is lowered into the sample deep enough to process another 50 L.
- The extractor is "recharged" with another 1000 mL of DCM.
- The procedure described above is repeated for as many times as necessary to process the entire sample.
- In processing the final sample aliquot, the solvent "recharge" should be adjusted to ensure that it will not overfill the extract container. Additionally, the sample probe should not be allowed to dip into any solid material which has settled to the bottom of the sample container. It is wiser to stop the process even if a few litres of sample are left as this exercise is not strictly quantitative and severe damage to the sample pumphead may occur if abrasive sediment is sampled.
- After use, the extractor should be cleaned and stored as described in (16,22).

TABLE A-I : Operating Conditions for Optimized Processing Technique

Sample	- degassed of supersaturated air @ room temperature - clarified by high-speed centrifugation.
Sample Input Rate (RPD-2CSC)	- 1000 mL/min, Setting 10 (maximum) on Sample Pump
Solvent Compensation (RPSY-2CSC)	- 13 mL/min, Setting 8 on Solvent Compensation Pump
Stirring Speed	- Setting 4-5 (Fisher "Stedi-speed" stirrer).
Sample Preheating (if used)	- Dependent on sample temperature. (See (17)).

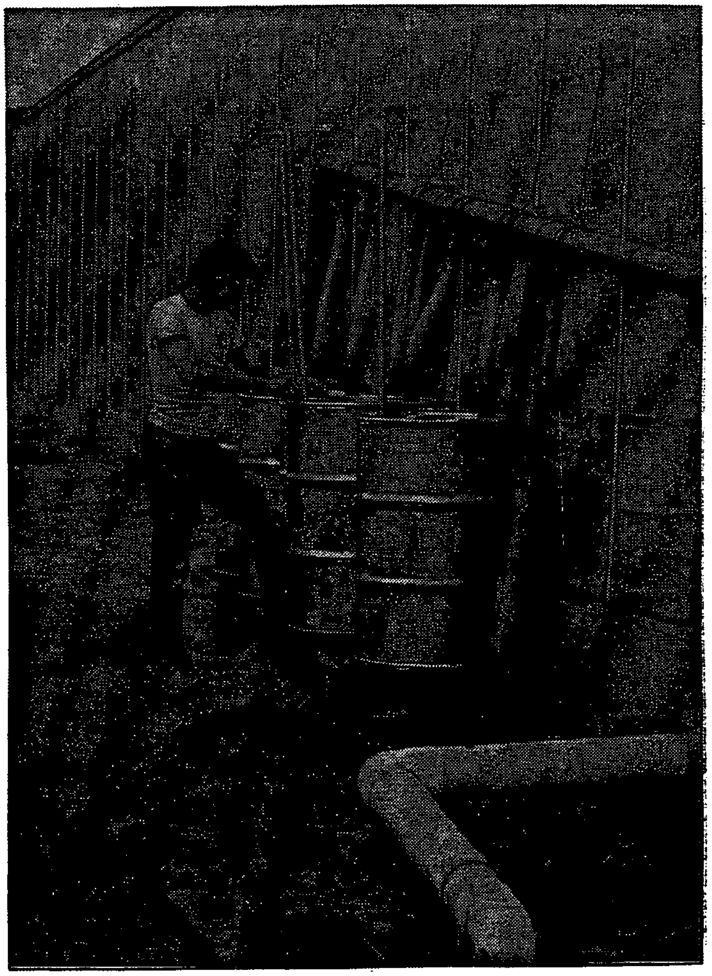


Figure 1: Sequential Sample Collection Arangement

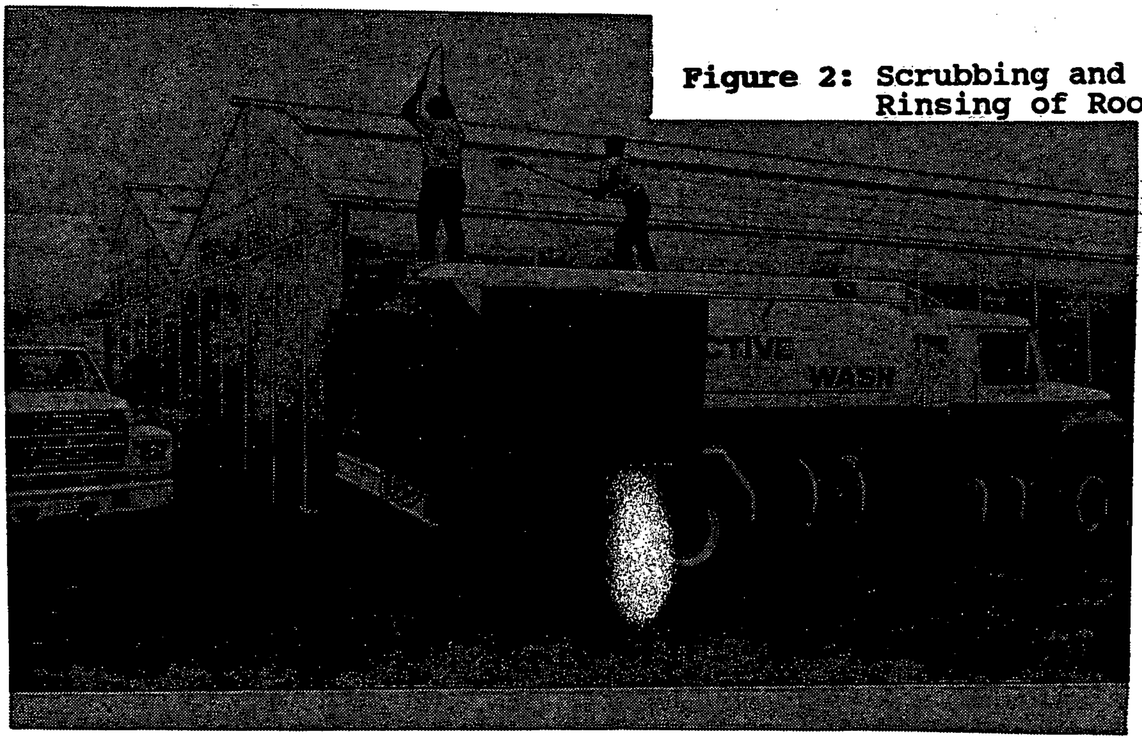


Figure 2: Scrubbing and High Pressure Rinsing of Roof Surface

Figure 3. Sample Processing Set-up

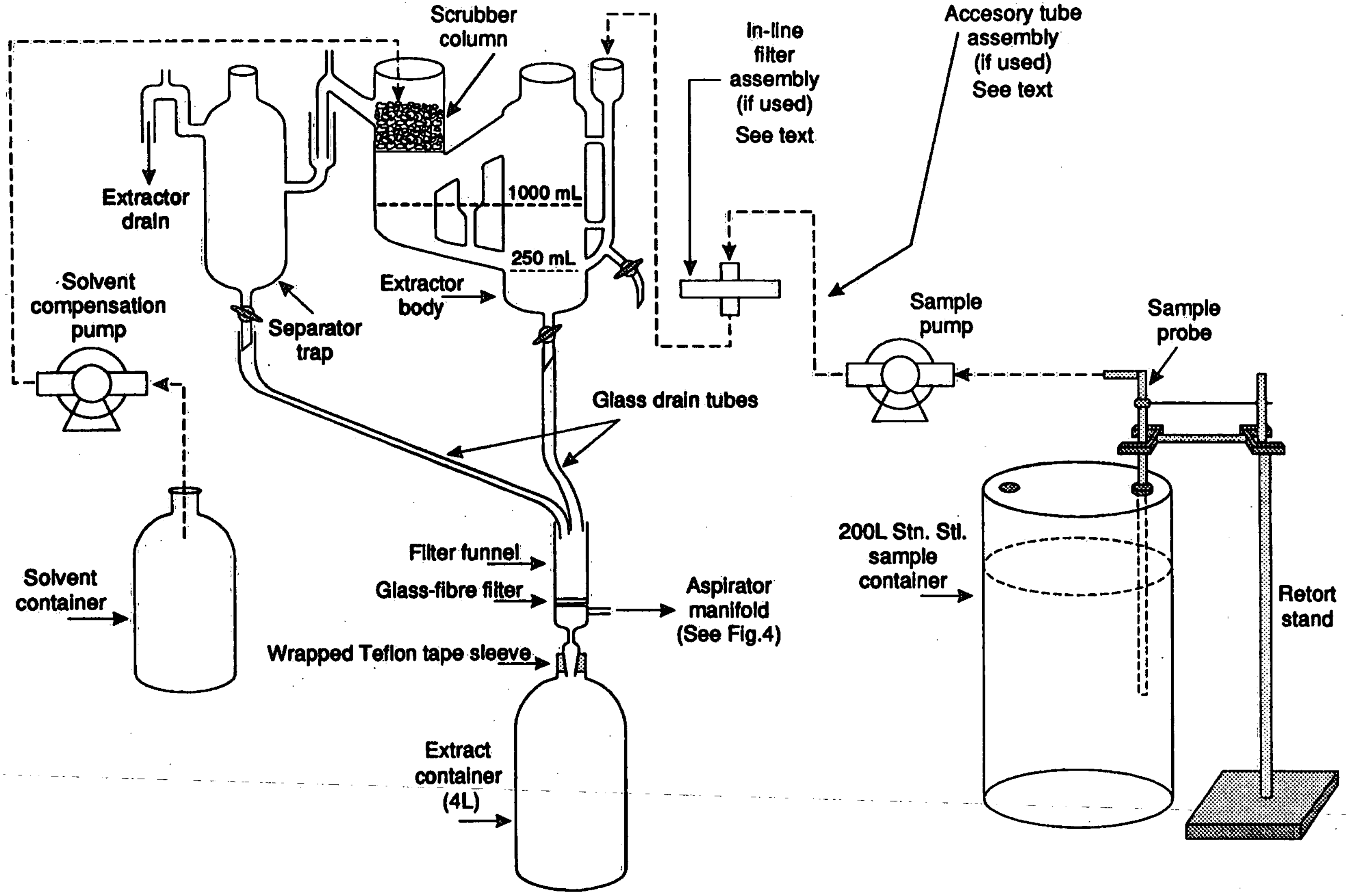


Figure 4. Aspirator Manifold

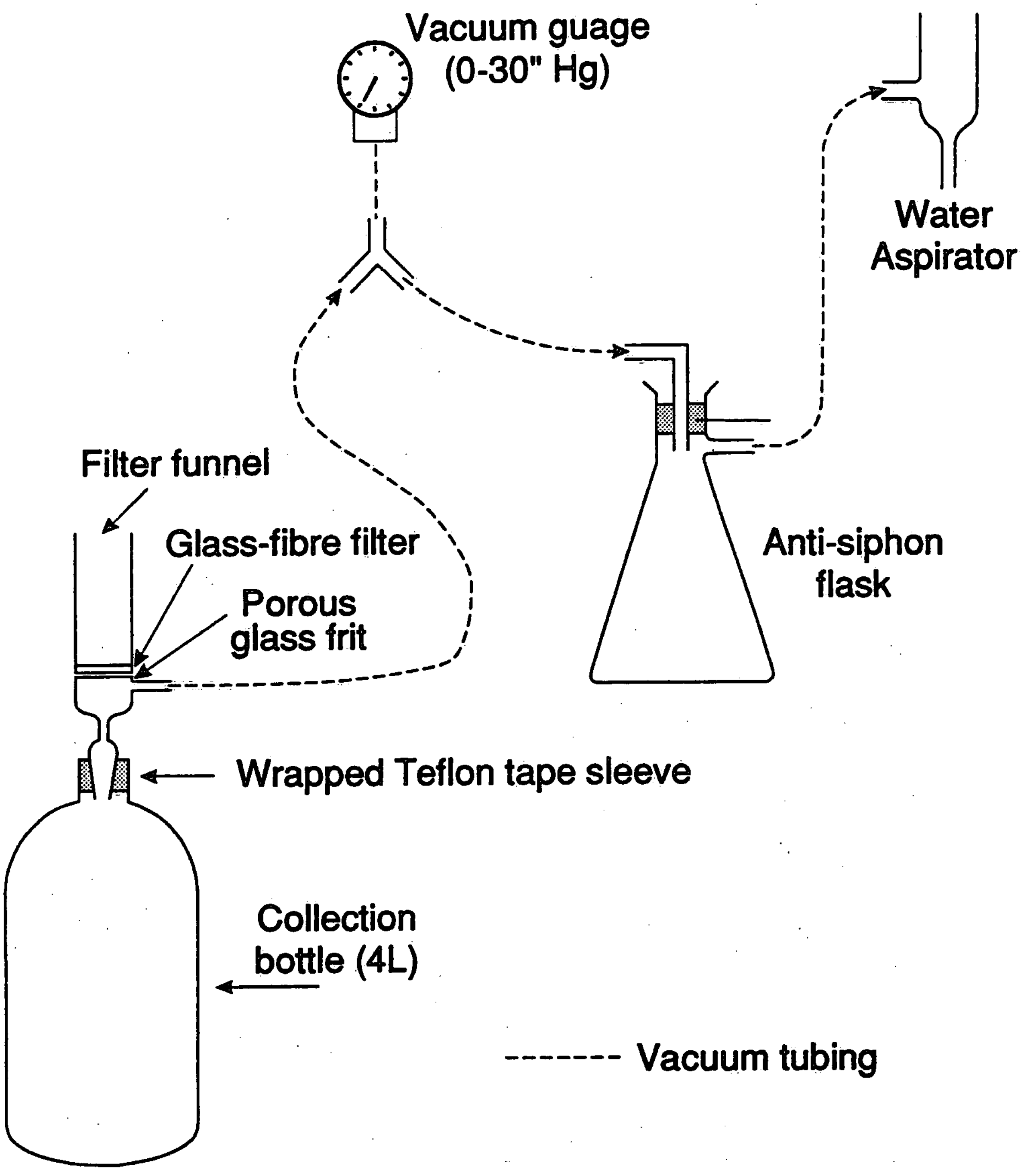
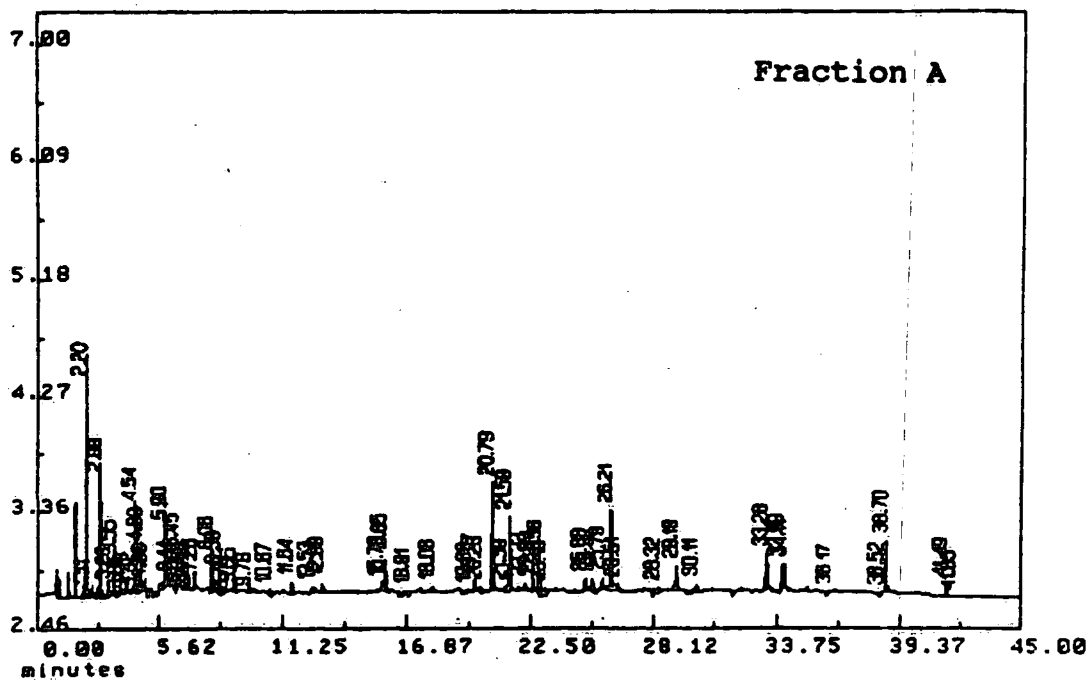


FIGURE 5 a : GC/ECD Chromatogram of Solvent Blank II

(Reference Table I,II)



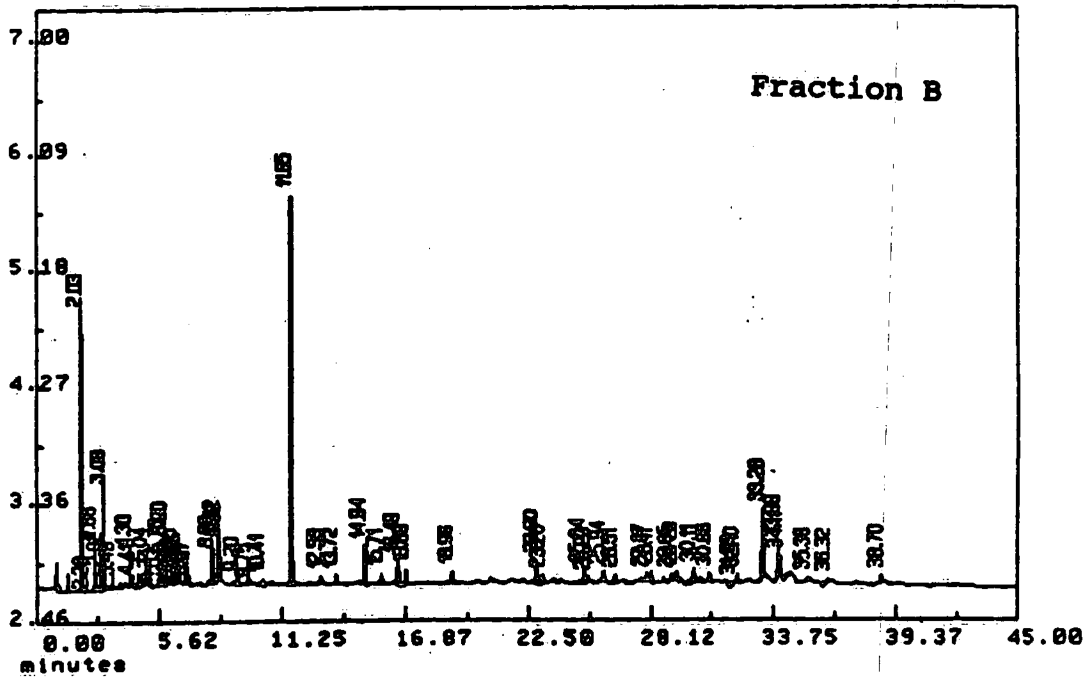


FIGURE 5 b : GC/ECD Chromatogram of Process Blank (MQ2 water)

(Reference Table I,II)

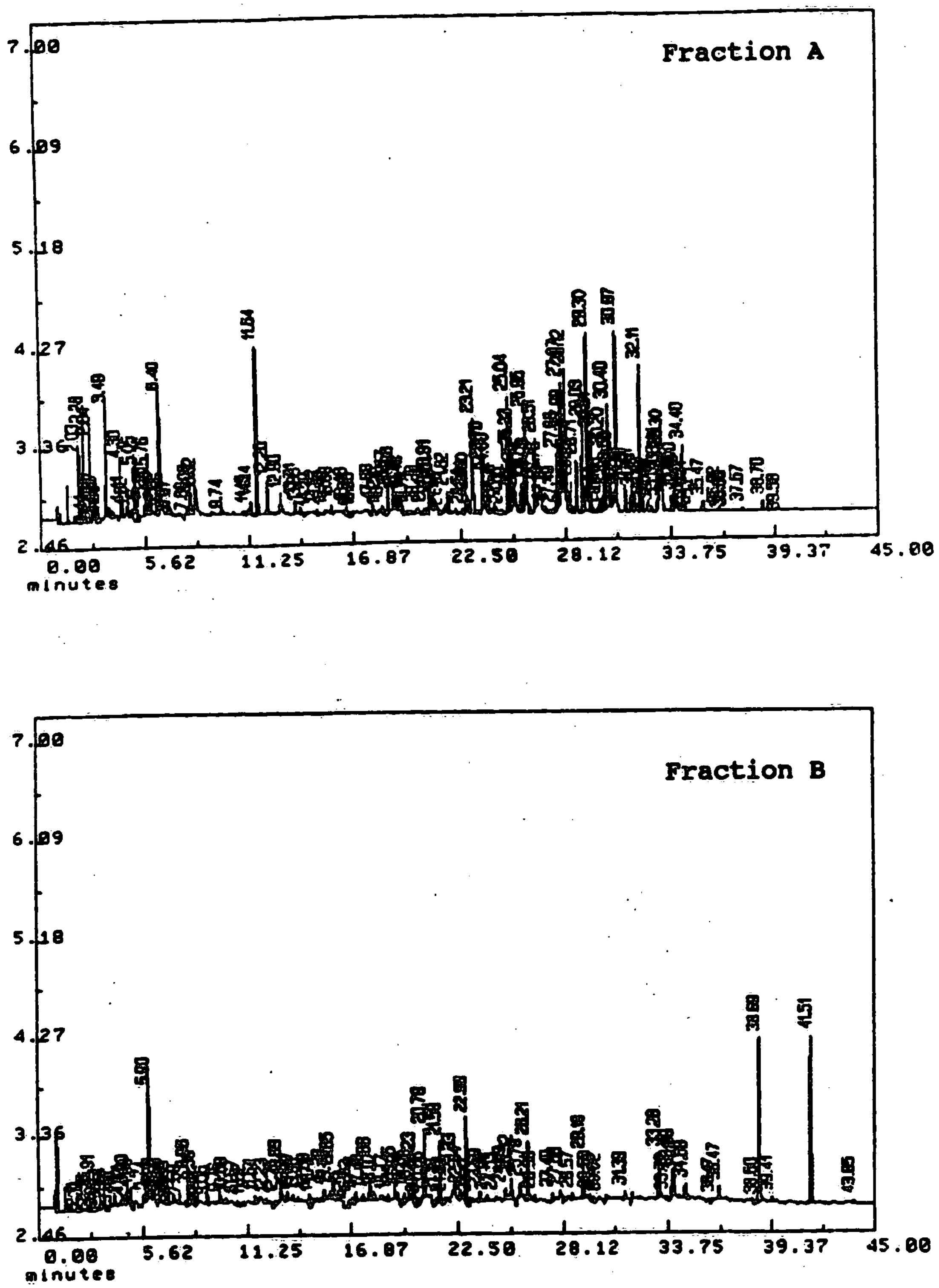


FIGURE 5 c : GC/ECD Chromatogram of Rainwater Sample 1

(Reference Table III)

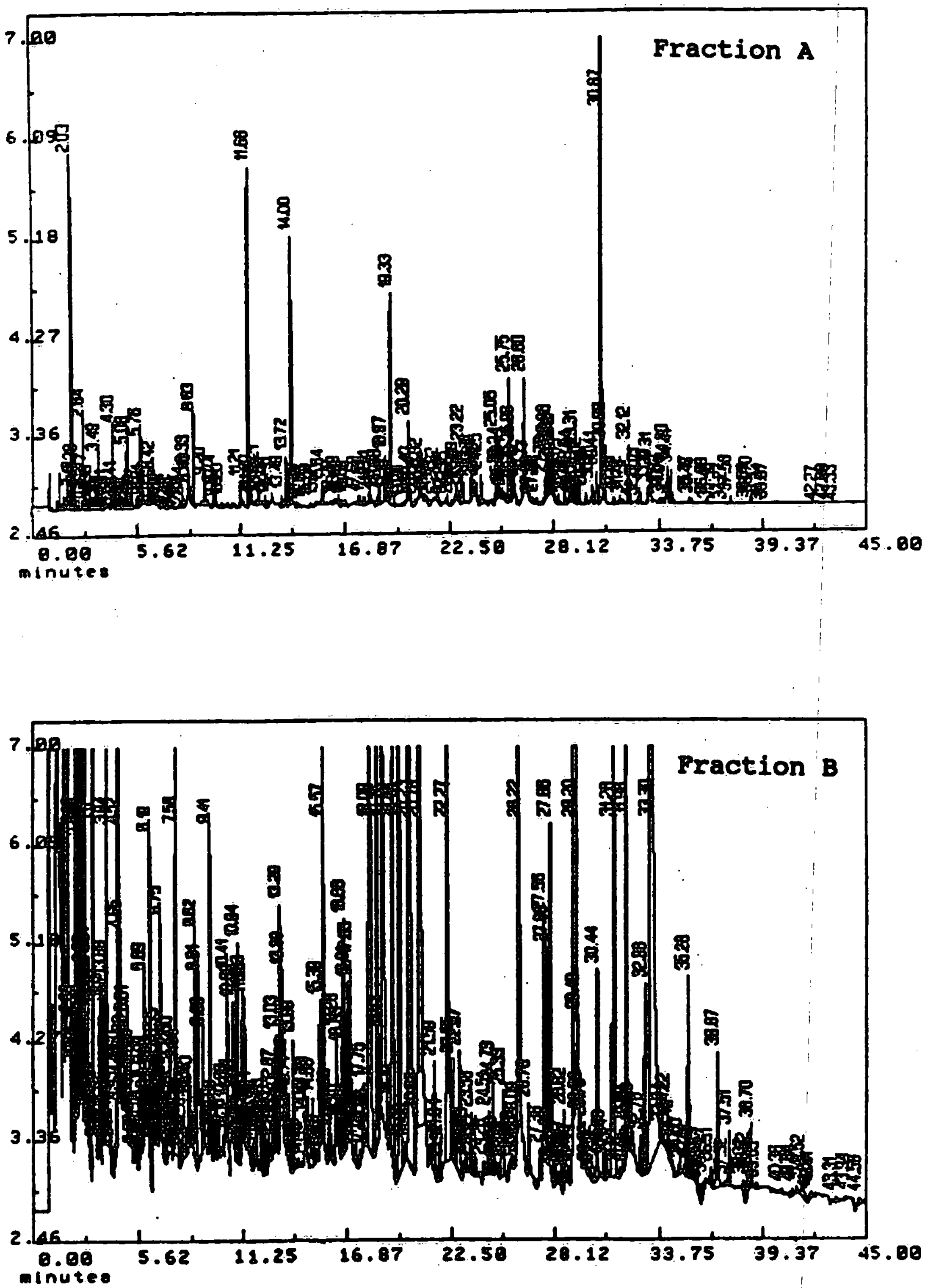


FIGURE 5 d : GC/ECD Chromatogram of Rainwater Sample 2

(Reference Table III)

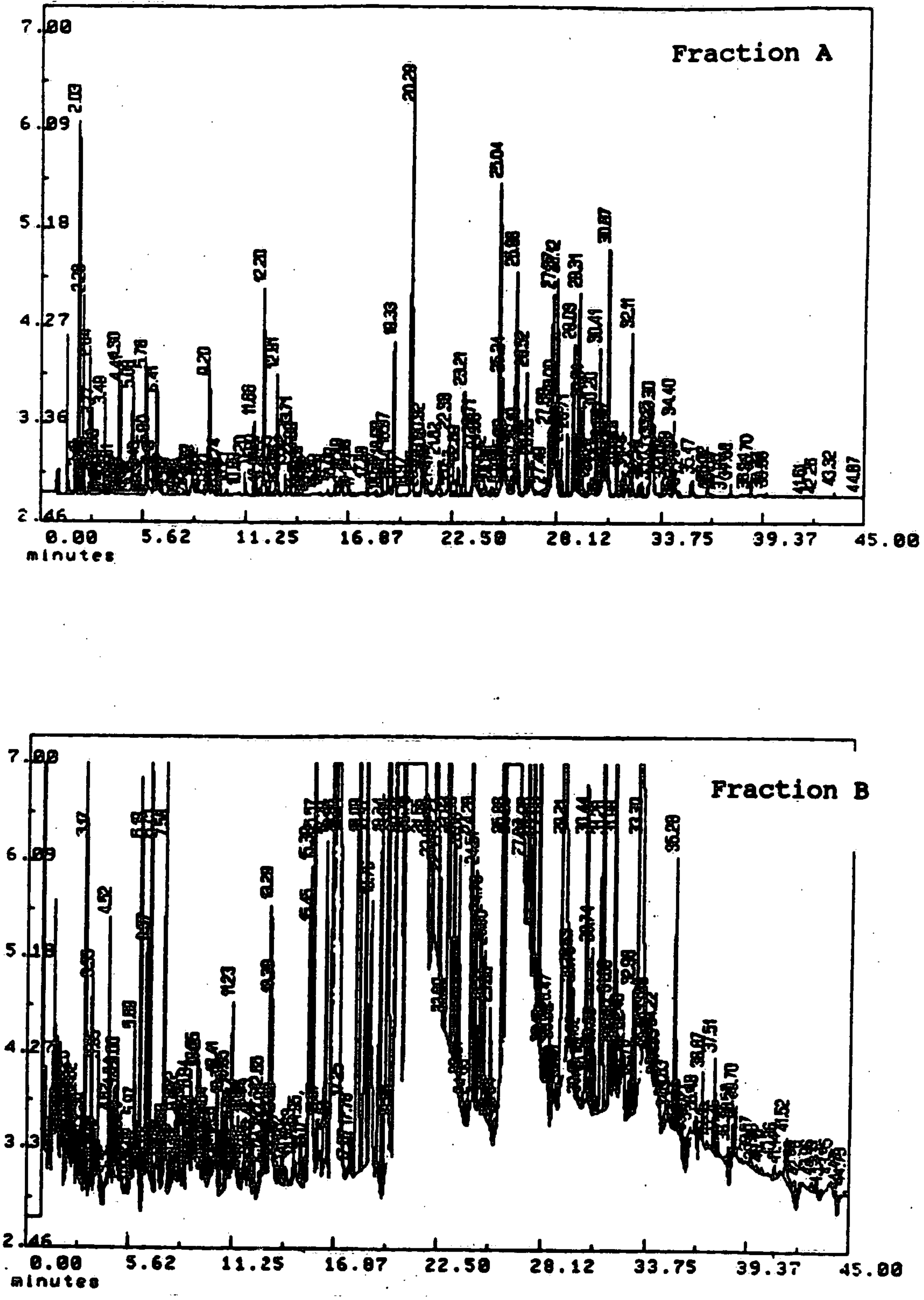


Figure 6 : TI Chromatograms of QC Blanks (PAHs)

(Reference Tables I,V)

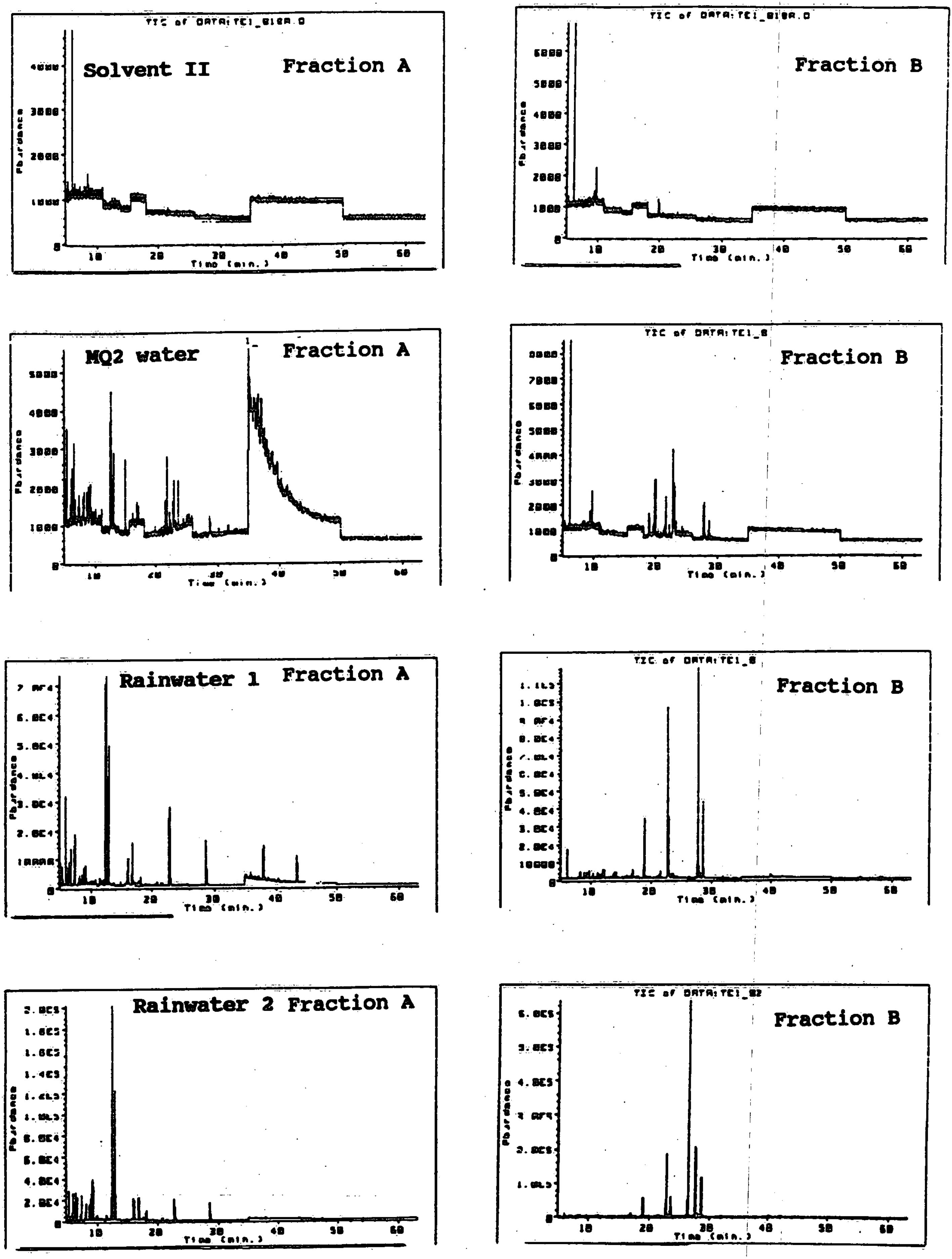


TABLE I: QC Sample Information

Type	Description	Comments
Solvent Blank I	300 mL DCM poured directly from reagent bottle to 500 mL rb flask for evaporative concentration. Triplicate samples.	Estimation of solvent contribution to final 200 mL QA/QC aliquots.
Sample Container Blank	30 mL DCM used to rinse sample containers for final 200 mL aliquots. Triplicate samples.	Compare with Solvent Blank I to estimate effectiveness of container cleaning procedure.
Extraction Blank	300 mL DCM from extraction of 20 L of MQ2 "organics-free" water.	Compare with Solvent Blank I to estimate contribution of extractor to process blank.
"Organics-free" water MQ2 blank	400 mL DCM extract of 200 L MQ2 "organics-free" water.	Estimation of degree of contamination of MQ2 water plus sum of other sources.
Barrel-cleaning Blank	300 mL DCM from extraction of 20 L of MQ2 "organics-free" water used as final rinse of rainwater containers.	Compare with Solvent Blank I, Extraction Blank and Container Blank to evaluate barrel cleaning procedure.
Solvent (50 L extraction) Blank II	1650 mL DCM	Estimation of solvent contribution to contamination in processing a 50 L rainwater sample. Compare with Solvent Blank I.

TABLE II : "Target" Compounds Determined in QC Blanks (Table I), (ng / sample)

Fraction "A" / Fraction "B" CBs and OCs, (ref. (20))

Compound	iso-octane (GC blank)	solvent blank I	solvent blank II	container blank	barrel blank	extractor blank	MQ2 water blank
1,2-dichlorobenzene	nd	1.05	3.2	nd	5.4	1.7	3.4
1,3-dichlorobenzene	nd	0.10/0.14	/5.2	nd	nd	nd	6.1
1,4-dichlorobenzene	nd	114/110	7.3	6.4/1.5	8.1/1.4	8.0/1.3	3.5/1.1
1,2,3-trichlorobenzene	5.5	nd	2.0/2.8	6.6/14.0	6.9/8.1	/9.7	0.13/7.8
1,2,4-trichlorobenzene	nd	nd	0.03	0.02/0.06	0.05/0.05	/0.04	0.04
1,3,5-trichlorobenzene	nd	nd	nd	nd	nd	/0.25	/0.46
1,2,3,4-tetrachlorobenzene	nd	0.19	0.28	0.2/0.18	nd	nd	0.25/0.46
Pentachlorobenzene	nd	nd	2.6	nd	0.31	nd	0.45/0.16
Hexachlorobenzene	nd	nd	3.0	nd	0.45	0.19	0.76
Heptachlor	nd	0.46	nd	0.50	0.84	0.64	1.5
Aldrin	nd	0.30	nd	0.17	0.32/0.44	0.88/0.60	1.1/0.59
p,p'-DDE	nd	0.73	nd	0.66	0.67/0.23	0.52	1.7
p,p'-TDE	nd	nd	nd	nd	/0.46	nd	0.70
p,p'-DDT	nd	1.19/3.26	1.2/1.2	0.99/1.10	/1.14	0.53/2.4	0.87/1.1
Mirex	nd	/0.21	nd	nd	nd	/0.30	/0.77
1,3-dibromobenzene **	nd	nd	nd	nd	nd	nd	nd
1,3,5-dibromobenzene **	nd	nd	nd	nd	nd	nd	nd
1,2,3,4-tetrabromobenzene **	nd	nd	nd	nd	0.09	nd	0.16/0.07
Number of compounds detected :	10	82/74	52/57	70/74	83/44	61/80	113/93

* - not detected, ** - surrogate standard compounds (ref. (20))

TABLE III : "Target" Compounds Determined in Rainwater Samples from First Collection (ng / sample)

Fraction "A" / Fraction "B", CBs and OCs (ref. (20))

Compound	Sample 1	Sample 2
1,2-dichlorobenzene	3.3/30.4	15.4/21.0
1,3-dichlorobenzene	4.5	7.5
1,4-dichlorobenzene	/6.3	4.6/8.7
1,2,3-trichlorobenzene	1.2/14.0	2.3/6.9
1,2,4-trichlorobenzene	/4.1	0.05/0.33
1,3,5-trichlorobenzene	/4.5	/1.3
1,2,3,4-tetrachlorobenzene	0.91/1.9	1.3
Pentachlorobenzene	1.8	2.5
Hexachlorobenzene	nd *	nd
Heptachlor	6.9	1.5
Aldrin	5.0	0.68
p,p'-DDE	nd	1.7/1.1
p,p'-TDE	/1.8	nd
p,p'-DDT	nd	nd
o,p'-DDT	1.4	1.2
Mirex	nd	nd
1,3-dibromobenzene **	0.32/8.4	nd
1,3,5-tribromobenzene **	nd	0.39
1,2,3,4-tetrabromobenzene **	2.3/5.5	1.6/4.4
Number of compounds detected :	147/201	155/195

* - not detected, ** - surrogate standard compounds (ref. (20))

TABLE IV : "Target" Compounds Determined in QC Blanks (Table I) and Precipitation Samples from First Collection (PAHs, (ref. (20)), (ng / sample).

Compound	solvent blank I	solvent blank II	container blank	barrel blank	extractor blank	MQ2 blank	sample 1	sample 2
Indene	nd *	nd	nd	nd	nd	5.7	22.2	71.0
Naphthalene	nd	nd	nd	nd	nd	3.3	22.7	136
2-methylnaphthalene	nd	nd	nd	6.9	nd	11.6	242	686
1-methylnaphthalene	nd	nd	nd	4.3	nd	6.8	163	409
-chloronaphthalene	nd	nd	nd	nd	nd	nd	nd	nd
Acenaphthalene	nd	nd	nd	nd	nd	nd	39.3	87.5
Acenaphthene	nd	nd	nd	nd	nd	nd	57.7	85.2
Fluorene	nd	nd	nd	nd	nd	nd	161	268
Phenanthrene	7.3	nd	6.1	19.2	5.7	31.1	846	1,402
Fluoranthene	4.2	nd	nd	7.3	nd	12.0	971	1,708
Pyrene	nd	nd	nd	8.1	nd	9.2	486	1,089
Benzo- -fluorene	nd	nd	nd	nd	nd	nd	192	85.7
Benzo-k-fluorene	nd	nd	nd	nd	nd	nd	7,919	1,601
Benzo-a-pyrene	nd	nd	nd	nd	nd	nd	nd	nd
Indenopyrene	nd	nd	nd	nd	nd	nd	76.2	nd
Benzo-ghi-perylene	nd	nd	nd	nd	nd	nd	nd	nd

* - not detected

TABLE V : Analytical results from Second Rainfall Collection (30,000-fold overall concentration).

Compound	Analytical Response (ng/sample)	
	Sample	Solvent Blank (***)
<u>Chlorobenzenes (CBs)</u>		
1,3-Dichlorobenzene	nd *	nd
1,4-Dichlorobenzene	43.38	nd (24.66)
1,2-Dichlorobenzene	14.67	nd
1,3,5-Trichlorobenzene	nd	nd
1,2,4-Trichlorobenzene	3.12	nd (3.07)
1,2,3-Trichlorobenzene	1.13	nd (0.44)
1,2,3,4-Tetrachlorobenzene	0.68	nd (0.55)
Pentachlorobenzene	0.68	nd (0.84)
Hexachlorobenzene	0.82	nd (0.51)
<u>Organochlorine Pesticides and Industrial Materials (OC./PCBs)</u>		
a-BHC	62.20	1.01
g-BHC	190.40	nd (0.58)
Heptachlor	nd	nd
Aldrin	nd	nd
Heptachlor Epoxide	nd	nd
g-Chlordane	nd	nd

(continued ...)

TABLE V : continued

a-Endosulfan	nd	nd (1.66)
a-Chlordane	nd	nd
Octachlorostyrene	nd	ndm **
p,p’-DDE	1.91	nd
Dieldrin	nd	1.23
Endrin	135.80	nd
o,p’-DDT	19.90	nd
p,p’-DDE (TDE)	nd	nd
p,p’-DDT (DDP)	nd	nd
ß-Endosulfan	nd	nd (13.91)
Endrin aldehyde	nd	nd
Photomirex	nd	nd
Mirex	nd	nd
Methoxychlor	nd	nd
Hexachlorobutadiene	nd	nd
Hexachlorocyclopentadiene	nd	ndm (1.89)
PCB (total)	32.09	47 ± 22 (n=4) (58.53)
<u>PAHs</u>		
Naphthalene	416.90	ndm (12.60)
2-Methylnaphthalene	136.40	ndm (nd)
1-Methylnaphthalene	259.90	ndm (nd)
2-Chloronaphthalene	nd	ndm (nd)
Acenaphthylene	207.20	ndm (nd)

(continued ...)

TABLE V : continued

Fluorene	141.00	ndm (nd)
Anthracene	152.00	ndm (nd)
Phenanthrene	335.50	ndm (20.96)
Fluoranthene	217.10	ndm (nd)
Pyrene	140.70	ndm (nd)
Benzo(a)anthracene	nd	ndm (nd)
Chrysene	83.00	ndm (nd)
Benzo(b)fluor	nd	ndm (nd)
Benzo(k)fluor	nd	ndm (nd)
Benz(a)pyrene	nd	ndm (nd)
Indenopyrene	nd	ndm (nd)
Dibenzo(ah)anthracene	nd	ndm (nd)
Benzo(ghi)perelyne	nd	ndm (nd)
<u>Phthalates</u>		
Dimethylphthalate	803.50	ndm (nd)
Diethylphthalate	1320.00	ndm (49.93)
Di-n-butylphthalate	5813.50	ndm (1232.71)
Benzylbutylphthalate	1678.70	ndm (152.82)
bis-2-ethylhexylphthalate	14706.5	ndm (11516.2)
Dioctylphthalate	102.00	ndm (27.82)

(continued ...)

TABLE V : continued

Chlorophenols		
Phenol	nd	ndm (nd)
2,4-Dichlorophenol	nd	ndm (nd)
2,3-Dichlorophenol	nd	ndm (nd)
2,6-Dichlorophenol	nd	ndm (nd)
3-Methyl,4-chlorophenol	nd	ndm (nd)
2,3,5-Trichlorophenol	nd	ndm (nd)
2,4,6-Trichlorophenol	nd	ndm (nd)
2,4,5-Trichlorophenol	nd	ndm (nd)
2,3,4-Trichlorophenol	nd	ndm (nd)
3,5-Dichlorophenol	nd	ndm (nd)
2,3,6-Trichlorophenol	nd	ndm (nd)
3,4-Dichlorophenol	nd	ndm (nd)
3,4,5-Trichlorophenol	nd	ndm (nd)
Pentachlorophenol	nd	ndm (nd)
Neutral Herbicides		
Atrazine	nd	ndm (nd)
Metolachlor	425.40	ndm (nd)
2,3,7,8-Tetrachlorodibenzodioxin	ndm	ndm (ndm)

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* nd - not detected

** ndm - not determined. Between the time the solvent check was made and the rainfall was processed, the analytical laboratory had expanded its suite of analytes to include PAHs, phthalate esters, some neutral herbicides, and chlorophenols. Consequently, no solvent data were available for these classes of compounds. See ***.

*** - in lieu of solvent data for the compound classes PAHs, phthalate esters, some neutral herbicides, and chlorophenols, data from analysis of the MQ2 blank (Table I) has been used to demonstrate effects seen with the large preconcentration factors achievable with the GLSE technique. See text for discussion.

TABLE VI : Surrogate Standards Recoveries under Optimized Processing Conditions (Second rainfall collection, single sample)

Compound	Reference Response (n=5)	Sample Response (n=1)	% Recovery (*)
1,3,5-Tribromobenzene (TBB)	46 ± 8	26	57
1,2,4,5-Tetrabromobenzene	61 ± 5	43	70
δ-BHC	29 ± 7	33	114

(*) - uncorrected for losses in subsequent analytical processing (see text, Results and Discussion).

TABLE VII : Comparison of Contaminant Levels Determined in First and Last Collections of Second Rainfall Event (ng/sample).

Compound	First Collection	Second Collection
Organochlorine Pesticides *		
a-BHC	5.20	nd *
g-BHC	2.93	0.28
p,p'-DDE	0.41	0.67
p,p'-DDD	0.85	nd
o,p -DDT	0.38	nd
p,p'-DDT	1.62	2.09
Mirex	0.53	nd
Total peaks detected / identified:	50 / 7	7 / 3
Polychlorinated Biphenyl (PCB) Congeners **		
Hexachlorobiphenyl	0.24	nd
Number of Congeners detected:	26	8
Total peaks detected / identified:	54 / 26	19 / 8

Summary: The PCB congeners detected in these samples were determined at levels of 3 ng/mL and less with the majority being < 1 ng/mL. No great differences in congener concentrations in the two samples were observed.

---

* Compounds detected in a suite of 15 OCs. Chlorobenzenes (CBs) not included.

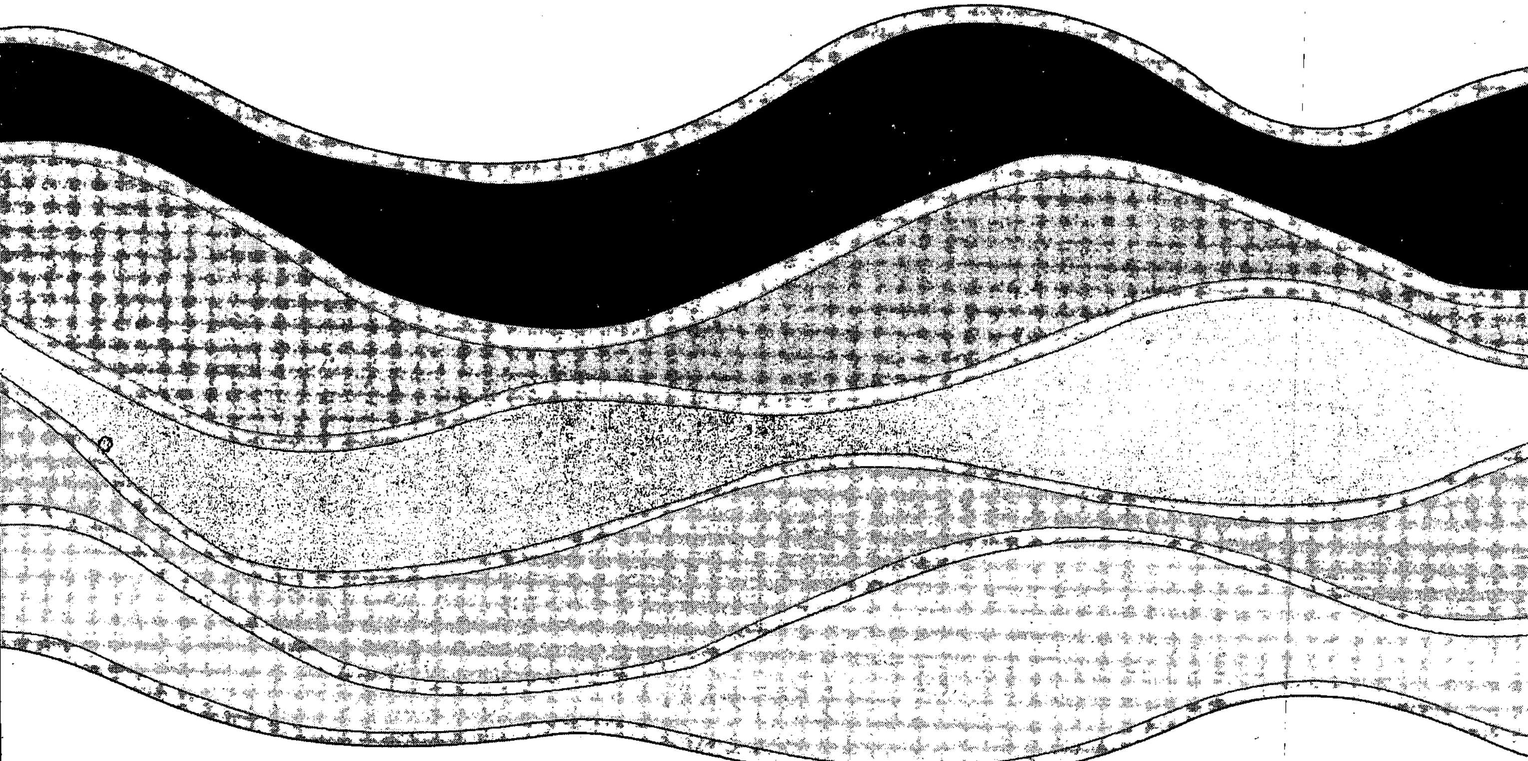
** Congeners detected in a suite of 63.

TABLE VIII : Analytical Results from First Rainfall Collection (5,000-fold overall concentration factor) *

Compound	Analytical Response (ng/sample)		
	Sample 1	Sample 2	Solvent Blank
Indene	26.02	26.64	nd **
2-Methylnaphthalene	51.44	41.78	nd
1-Methylnaphthalene	35.80	28.38	nd
Phenanthrene	90.34	95.84	nd
Fluorene	39.34	26.18	nd

* These represent the only compounds of a suite of 43 CBs, OCs, PCBs and PAHs which were detected with this overall preconcentration factor.

** nd - not detected.



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